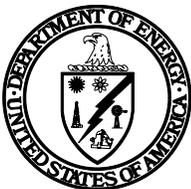


DOE/FETC-98/1071
(DE98002060)

A Partial Oxidation Technique for Fuel-Cell Anode Exhaust-Gas Synthesis

Randall S. Gemmen
Edward H. Robey, Jr.

October 1998



U.S. Department of Energy
Federal Energy Technology Center
Pittsburgh, Pennsylvania
Morgantown, West Virginia



FETC's Customer Service Line: (800) 553-7681
FETC's Homepage: <http://www.fetc.doe.gov/>

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Available to DOE employees and contractors from the Office of Scientific and Technical Information, P.O. Box 62, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices are available by phone: (423) 576-8401; fax: (423) 576-5725; or e-mail: reports@adonis.osti.gov.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

Abstract

This paper describes the performance of a gas generator used to synthesize the exhaust gas from the anode of a molten-carbonate fuel cell. The composition of this gas is estimated to be that of equilibrium at 1,250 °F and 1 atm: 48% CO₂, 39% H₂O, 5% CO, and 8% H₂, with an energy content of approximately 39 Btu/scf (higher heating value). To synthesize a range of gas compositions around this point, the gas generator partially oxidizes a mixture of CH₄, O₂, and CO₂ to generate energy densities between 20 and 60 Btu/scf at temperatures between 1,198 and 1,350 °F. Results show that the technique provides a relatively high ratio of CO to H₂ concentrations compared with the target composition (CO:H₂ of 2, versus 0.71). A detailed chemical model shows that the likely cause is quenching of the CO and H₂ chemistry below 2,000 °F.

Acknowledgment

The authors would like to express their thanks to Rick Addis for his support and technical expertise in constructing and running the gas generator.

Contents

Introduction	6
Experimental Description	7
Gas Generator Description	7
Oxygen and CO ₂ Distribution System	8
Operation	9
Light-Off	9
Transition	10
Normal Operation	10
Experimental Results	11
Model	13
Conclusions	15
References	16
Figures	17
1. General View of the B27 Gas Generator	17
2a. View of the B27 Gas Generator Nozzle	18
2b. Detail of Internal Nozzle Geometry	18
3. Gas Generator Pilot Tube and Swirl Vane	19
4. Schematic of Gas Generator	19
5. Schematic of Gas Generator Oxygen and Carbon Dioxide Supplies	20
6a. Flow Rate History of a Typical Run	21
6b. Temperature History of a Typical Run	21
7. Product Gas Composition Versus Fuel-to-Oxygen Ratio	22
8. Ternary Plot of Product Gas Compositions (Volume Basis, Dry)	23
9. Water Vapor Content of Product Gases	23
10. Energy Content (Wet Basis) of Product Gases	24
11. Numerical Model Description	24
12. Model Results Showing Quenching of CO and H ₂ Inside the Gas Generator	25
13. The Effect of Heat Rate on CO and H ₂ Predictions	25
Tables	26
1. Initial Valve Settings for the Gas Generator Nozzle	26
2. Transition Steps from Start-Up to Normal Gas Generator Operation	27
3. Analysis of Product Gas Composition	28
Appendix	30

Introduction

There are a variety of methods for producing a synthesis gas (syngas) of desired composition, temperature, and pressure, e.g., autothermal converters, catalytic/steam reforming, and partial oxidation techniques. This paper presents a gas generator system used to produce a syngas to simulate the energy densities found in the off-gas from the anode of a molten-carbonate fuel cell. These fuel cells operate at about 1,250 °F, with anode off-gas energy densities of about 40 to 50 Btu/scf (Carlson 1997). The composition of this gas is estimated to be that of equilibrium: 48% CO₂, 39% H₂O, 5% CO, and 8% H₂, with an energy content of approximately 39 Btu/scf (higher heating value). The partial oxidation technique was selected for this gas generator system. This system provided a range of fuel energy densities with nearly fixed H₂:CO ratios at temperatures between 1,198 and 1,350 °F. To further understand the performance of this system, a detailed kinetics model of the system was executed and its results were compared to the experimental data.

Experimental Description

Gas Generator Description

A gas generator is used to create a low heating value gas, consisting of water vapor, CO₂, CO, and H₂, through the incomplete combustion of natural gas in an atmosphere of O₂ and CO₂. Liquid O₂ and liquid CO₂ Dewars supply O₂ and CO₂ gas at baseline flow rates of 386 scf/h (182 slpm) and 289 scf/h (136 slpm), respectively. These gases are mixed with natural gas at a baseline flow of 225 scf/h (106 slpm) in a nozzle, and are burned inside a water-cooled combustor. A general view of the gas generator is shown in Figure 1. The gas generator combustor is composed of a carbon steel vessel lined with approximately 1 inch (25.4 mm) of Plicast 40 refractory (i.d. 10.6 inches (0.27 m)) and wrapped outside with copper cooling coils. The axial dimension inside the combustor is approximately 34 inches (0.864 m). The vessel is suspended from above by a steel framework. Gas supplies enter the gas generator through the nozzle on top, react inside the vessel, and exit the reactor through a 2 inch (51 mm) port on the bottom left. A sight glass on the bottom flange of the vessel provides optical access. In a typical application, a video camera is focused through the sight glass to transmit an image of the flame to the control room. A flame detector and a thermocouple are tied to a safety interlock system to automatically shut off the fuel and O₂ if the flame goes out.

A general view of the nozzle arrangement is shown in Figure 2a, and a detailed view of the nozzle internal geometry is shown in Figure 2b. The body of the nozzle is composed of a section of 1-inch schedule-40 carbon steel pipe. A length of 1/2-inch (13 mm) diameter stainless steel tubing is located in the center of the pipe to act as a concentric pilot. A 1/4-inch (6.35 mm) ceramic tube containing a 1/16-inch (1.59 mm) stainless steel electrode enters the pilot tube through a cross fitting on the top, and extends down the center to within 1.25 inches (32 mm) of the end of the nozzle. Fuel (natural gas) is delivered through a tube shown on the left side of the figure and branches into two paths, one leading to the cross on the top of the pilot tube and the other leading to the main annulus fitting on the top left of the 1-inch pipe. The relative flow split between pilot fuel and main fuel is controlled by adjusting flow control valves (FCVs) 30 and 31, respectively. The combustion air for the nozzle also enters on the left side (Figure 2), and splits into main and pilot streams, which are controlled by FCVs 32 and 33, respectively. These lines pass around the rear of the nozzle and meet their respective O₂/CO₂ mixture streams before entering the pilot tube and main annulus. O₂ and CO₂ supplies enter from the right side (Figure 2), mix, and split into main annulus and pilot streams. The relative flow splits of main and pilot O₂/CO₂ mixtures are controlled by setting FCVs 32 through 35. As previously indicated, these flows meet and mix with the main and pilot air streams prior to entering the nozzle.

The main air/O₂/CO₂ mixture mixes with the main fuel stream as it passes down the annulus defined by the 1-inch outer pipe and the 1/2-inch pilot tube. The main flow is further mixed and made uniform when it passes through a 1-inch (25.4 mm) section of densely packed steel window-screen approximately 6.5 inches (0.165 m) from the downstream end of the nozzle. It is then swirled by passing over five 45-degree flat swirl vanes (Figure 3). In order to reduce the likelihood of a flashback in the nozzle, the main flow is accelerated by a reduction of cross-

sectional area created by attaching a 0.745-inch (19 mm) o.d. sleeve to the pilot tube and inserting a sleeve in the 1-inch pipe to reduce its inside diameter to 0.950 inch (24 mm). The steel sleeve added to the pilot tube also has five swirl vanes to maintain the swirling flow. Gas velocity in the annulus between the sleeves is approximately 91 ft/s (28 m/s) at baseline flows. A thermocouple is inserted into the annulus above the upper swirl vanes and is tied into an alarm to warn operators of flashback events. The tip of the steel pilot sleeve originally tapered toward the end of the pilot tube, but after some initial trial and error, it was replaced with a 0.725-inch diameter (18 mm), 1.694-inch (43 mm) long ceramic TIG torch cup to make it more durable. The ceramic tip can become quite hot (frequently glowing white-hot) and over a year of operation has sustained some damage, which can be seen in the figure.

Some of the other pertinent features of the gas generator are shown in Figure 4. In addition to the air, fuel, O₂, and CO₂ supplies entering through the nozzle, other inputs include purge air (to reduce condensation on the sight glass), and cooling water. The purge air mixes/reacts with the product gases, and must be turned off when synthesizing the anode gas. The cooling water does not mix with the reactants. Its purpose is to limit the shell temperature of the gas generator and, to a degree, control the temperature of the product gases. Four separate cooling zones exist inside and outside the vessel. A portion of a cooling coil wrapped around the bottom of the nozzle can be seen in Figure 2. Two type-R thermocouples are used to monitor the temperature of the process: (1) TE-012 is used to monitor the flame and is tied to the safety interlock system, and (2) TE-927 is used to measure the temperature of the product gases leaving the gas generator. Not shown are three thermocouples used to monitor the vessel wall temperature. A slip stream of the product gas is withdrawn approximately 10 ft (3.05 m) downstream of the gas generator for analysis. The bulk of the gas passes on to a 10 ft-long (3.05 m) development combustor used to investigate oxidation strategies for the low Btu gas mixture. The gas then mixes with dilution air, after which it passes out a 20 ft (6.1 m) stack.

Oxygen and CO₂ Distribution System

Because of the unique requirements of using pure oxygen in combustion systems, the general facilities used in this project will be described, with particular attention given to the oxygen and carbon dioxide systems.

Feedstocks for the gas generator include combustion air (for start-up only), natural gas, O₂, and CO₂. The air and natural gas are taken from FETC's standard facilities (the 700 psia (4.8 MPa) air system and the 50 psia (0.34 MPa) natural gas system). O₂ and CO₂ are supplied from Dewars of liquid O₂ and liquid CO₂ stored in a shed located near the project area. Two Dewars of each gas provide sufficient supplies for a week at our normal test schedule (i.e., about three 8-hour days of operation per week). As shown in Figure 5, the CO₂ Dewars are manifolded together. This manifold draws gas from the Dewar with the highest pressure, and includes a regulator for the supply pressure. Gaseous CO₂ is provided from the manifold at a pressure of approximately 100 psig (0.69 MPa). The temperature of this gas can be quite low (e.g., -50 °F (-45 °C)), but it is heated to approximately 80 °F (27 °C) by a heater constructed of six passes (i.e., three loops) of flow tubing bundled together with four 6-ft resistance heating elements (500 W each).

The O₂ system is similar to the CO₂ system except that (1) it is constructed of rigid copper tubing and brass fittings, (2) all parts were specially designed and cleaned for O₂ service, (3) the manifold includes a heat exchanger to help vaporize the O₂, and (4) both the gas and the liquid ports of the Dewars are used in order to provide enough flow. A heater is provided to warm the oxygen, but it is rarely needed.

Operation

Light-Off

The gas generator is lit-off with air and natural gas and is operated for a period of time to warm it and any downstream applications prior to making the transition to O₂/CO₂/fuel operation. The light-off process is easily accomplished if the flow split between the pilot and main gas mixtures is properly set. The flow splits are controlled by the settings of FCVs 30 through 35. Initial settings for these valves are shown in Table 1. Any deviation from these settings, or any alteration of the nozzle that would alter the pilot/main flow splits, can make the gas generator difficult to light.

This section provides an overview of the light-off procedure. On many burners, the pilot flame is lit first and then the main fuel is brought on gradually until the main flame is established. The main air, pilot air, and fuel supplies for the gas generator are not metered and controlled separately, thereby requiring a different light-off strategy. To light the gas generator, the air flows are established, the spark is turned on, and then fuel is suddenly provided to the pilot and main streams, igniting both nearly simultaneously. The general procedure is as follows:

- Establish dilution air flow to the stack (10,000 scf/h (4700 slpm)).
- Establish combustion air flow (800 scf/h (377 slpm)).
- Engage the keyed shut-off (to enable the fuel solenoid and ignitor power).
- Set the fuel-flow controller in manual mode at a valve position setting that will provide 75 scf/h (35 slpm) natural gas when the fuel shut-off solenoid is opened.
- Turn on the ignitor toggle switch. Verify via the video monitor.
- Enable the fuel toggle switch.
- Depress and hold the start-up override button. This will open the fuel solenoid until the flame is established and the flame detector (peeper) and temperature interlocks are satisfied. The flame should ignite within several seconds of depressing the override button.
- Verify the presence of the flame visually on the video monitor and on the data acquisition computer by observing TE-012.
- Start the flame detector (peeper).
- When the temperature at TE-012 is well above 1,000 °F (537 °C), the override button may be released and the spark toggle switched off.

The gas generator can be left at these flows for an initial warm-up period, or the air and fuel may be increased in stages to 1,000 scf/h (471 slpm) air and 95 scf/h (45 slpm) fuel to

provide a more rapid warm-up. At air flows greater than 1,000 scf/h, the gas generator becomes somewhat unstable and is more likely to blow out.

Plots showing the gas flow rates and selected temperatures during the phases of light-off, transition, and normal operation of a “typical” run are shown in Figures 6a and 6b. The combustor was lit just after 8:15, after which the air and fuel flows were increased to 1,000 scf/h and 90 scf/h, respectively, for about 1/2 hour before beginning the transition to baseline conditions, which began at 9:30.

Transition

Through engineering judgement and trial and error, a procedure was developed to transition the gas generator from its light-off conditions on air and fuel to operation on O₂, CO₂, and fuel at “baseline” operating conditions. During the initial stages of the transition, the gas generator flame is sensitive to operating conditions, and is likely to blow out if conditions deviate much outside the plan. During the latter stages of transition, when the gas generator is consuming substantial quantities of oxygen, the flame is more stable. The steps for the transition are summarized in Table 2. Note that at step #31, the gas generator is consuming 386 scf/h (182 slpm) O₂, 289 scf/h (136 slpm) CO₂, 225 scf/h (106 slpm) natural gas, and 400 scf/h (189 slpm) air, plus the air from the sight-glass purge. The gas generator is usually left at this step for an hour or more to complete warm-up and to heat downstream experimental hardware. In the example run shown in Figures 6a and 6b, this warm-up interval extended from 9:45 to 11:10. When the systems have reached the desired temperatures, the sight-glass purge may be turned off and the 400 scf/h air removed from the gas generator. The gas generator will then be running rich, and production of low-Btu fuel will begin. Note that the temperature of the product gases will begin to fall after completing the transition (e.g., note the drop in product gas temperature at just before 11:15 in Figure 6b). Heat energy that was being released inside the gas generator prior to completion of the transition now leaves the gas generator in the form of chemical energy (unburned CO and H₂).

Normal Operation

After completing the transition to normal operation, the gas generator flame remains stable. For example, it will operate with fuel flow rates as low as 100 scf/h (47 slpm) without flaming out. This flexibility provides a means of varying the heating value of the product gas over a range of 0 to 70 Btu/scf (2.6 MJ/m³).

Temperatures measured about 6 inches (0.152 m) downstream of the flame are generally 2,200 to 2,300 °F (1,200 to 1,260 °C) (not corrected for radiation effects), while product gas temperatures are typically 1,500 °F (815 °C). In Figure 6b, the product gas temperature excursions above 1,500 °F (815 °C), occurring at 12:00 and 13:00, were caused by turning the sight-glass purge air on to provide excess oxygen to complete the oxidation, and thereby provide more heat to warm the downstream reactor. Gas generator shell temperatures are typically maintained at about 600 to 700 °F (316 to 371 °C), with cooling water venting as steam at approximately 217 °F (103 °C).

Experimental Results

The normalized dry-basis compositions of each sample of gas generator product gas are listed in Table 3. Neither O_2 nor CH_4 were detected in any significant amount for any of the samples analyzed. A few of these samples were collected while intentionally varying the O_2 , CO_2 , and fuel feedstocks in order to observe the effect on product gas, but most were collected while varying only the fuel (to vary the heating value of gas being provided to the other experimental rig). As a result, the majority of the data shows the effect of varying the fuel flow rate while the O_2 and CO_2 flow rates were held essentially constant at their baseline values of 386 and 289 scf/h (182 and 136 slpm), respectively. The data points where the CO_2 flow was not at baseline include 970513 #3 (baseline + 30% CO_2), 970513 #2 (baseline + 20% CO_2), 970513 #1 (baseline + 10% CO_2), 970513 #4 (baseline - 10% CO_2), 970513 #5 (baseline - 20% CO_2), and 970423 #4 (baseline O_2 , low fuel, low CO_2). Similarly, the data points where the O_2 flow rate was not at baseline include 970513 #7 (baseline + 7% O_2), 970513 #6 (baseline + 4% O_2), 970513 #8 (baseline - 4% O_2), 970513 #9 (baseline -8% O_2), and 970423 #6 (baseline CO_2 , low fuel, low O_2). The remaining 41 samples were taken at baseline settings of O_2 and CO_2 flow with a fuel flow rate varying from 197 to 240 scf/h (93 to 113 slpm). Note also that H_2 data was not taken for several data points from test 971104. The CO and CO_2 values for these points, identified by shading in the table, are not normalized.

The trends in product gas composition with respect to the amount of gas generator fuel are shown in Figure 7. The relative amount of gas generator fuel is expressed by the fuel-to-oxygen ratio. The data spans a fuel-to-oxygen ratio of 0.52 to 0.64 (corresponding to equivalence ratios of approximately 1.04 to 1.28). The bulk of the data comes from those cases where the gas generator fuel was varied. The other two portions of data with off-baseline values of O_2 and CO_2 flow (as discussed above) are identified by distinct symbols. Trend lines are drawn through the fuel series data for each species. As the feed to the gas generator was made richer, the relative quantities of H_2 and CO increased, while CO_2 decreased. The off-baseline data for O_2 and CO_2 flow rates do not appear to deviate from their trend lines by more than the natural variation in the measurements.

The relative composition of the three dry-state gaseous species can be represented as a point on a ternary component plot as show in Figure 8. Data points falling near the left corner of this plot represent gas mixtures consisting primarily of CO_2 , points toward the right corner represent larger proportions of H_2 , and those near the apex are mostly CO. The gases produced by the gas generator consisted largely of CO_2 , with increasing amounts of CO and H_2 as the fuel-to-oxygen ratio increased. Data points with off-baseline CO_2 and O_2 flow rates fell essentially on the same trend line. Product gases with CO as high as 30% and H_2 as high as 10% were produced. Also included on this figure is a point showing the composition of a “typical” fuel-cell anode exhaust-gas predicted by equilibrium models ($H_2:CO = 1.411$). This was our initial target composition for the gas generator product, but none of the variations attempted in feedstock flow rates, cooling-water flow rates, and pilot/main feed-mixture split moved the product gas composition off the trend line toward the target. The product gas had relatively more CO and less H_2 than desired.

Although we could not match our initial target for gas composition, we could alter the product gas composition to match a target energy density (heating value). Dry-basis heating values can easily be inferred from the data in Figure 8. The heating values of CO and H₂ are similar, averaging approximately 330 Btu/scf (12 MJ/m³). Thus, the diagonal grid lines parallel to the CO-H₂ boundary line represent approximately equal heating values, ranging from 330 Btu/scf on the right to 0 Btu/scf at the lower left corner. The heating value of product gases plotted on this figure vary from 33 to 132 Btu/scf (1.2 to 4.9 MJ/m³) on a dry basis.

In order to express the heating value of the product gases on a wet basis, it was necessary to estimate the quantity of water vapor. This was done by using material balance calculations to balance the mass flow rate of oxygen entering (as O₂ and CO₂) and leaving (as CO₂, CO, and H₂O) the gas generator. A QuickBASIC program was written in which a subroutine calculated the oxygen mass-balance error as a function of the volume fraction of water vapor in the product gas. A bisection routine was then used to solve for the amount of water vapor. The program is attached as an Appendix. The calculations showed that the product gas averaged around 46% water vapor by volume with a slight decreasing trend as the fuel-to-oxygen ratio was increased. Figure 9 shows these results, along with a least-squares fit line through the data. The wet-basis heating values of the product gases are shown in Figure 10. As the fuel-to-oxygen ratio was increased, the heating value of the product gases increased. In many of our experiments, it was necessary to know the energy content of the gas generator product, but there was insufficient time to take a complete gas sample. For these instances, we relied on the empirical correlation of energy content with the fuel-to-oxygen ratio. This correlation was based on gas sample data from tests 970423 through 970530, and is represented by the dashed line in Figure 10. This equation provided an adequate fit to the original data, as well as subsequent data taken to periodically validate the gas compositions and energy densities.

Model

A simplified combustor model employing detailed chemical kinetics was used to analyze and predict the performance of the gas generator system. The main goal of the study was to understand the cause for the high CO level, relative to equilibrium, over the range of temperatures studied (1,350 to 1,980 °F (732 to 1,082 °C)). The model considers the detailed evolution of the fuel species inside the partial oxidation combustor, which consists of a series of plug-flow-reactor sections (see Figure 11). Following the usual definitions, for each plug-flow-reactor, the system is considered to be one dimensional and nondiffusive.

For this work, 30 plug-flow-reactor sections were used. The first reactor was supplied with pre-reacted O₂, CO₂ and CH₄ at the same ratios and total flow used during experimental syngas generation. The temperature of the inlet gas was set at 5,000 °F (2,760 °C) in order to replicate the thermal energy in the initially reacted gas. This compares well to the adiabatic combustion state and the experimental data, showing that nearly all of the reaction inside this high oxygen environment occurs within the first 2 to 3 inches of the top of the gas generator. As will be seen, these temperatures are high enough to provide quick equilibrium among all species used in the reaction mechanism. Therefore, this modeling technique provides a meaningful way to study the history of each species, and to approximate the chemical processes inside the gas generator as the gases cool and the chemistry becomes “quenched.”

To approximate the removal of heat from the system, some quantity of heat is removed at the inlet to each combustor section by dropping the temperature a given amount. The mixture then reacts according to typical plug-flow chemistry until the mixture leaves the combustor section. The simulation uses the reaction set from Kim et al. (1991), which has 12 species, and the thermodynamic data from the Chemkin database (Kee et al. 1989). Because of the parabolic mathematical nature of the proposed model, the solution of the problem is achieved by starting at the first combustor, and then sequentially assessing the solution for each downstream combustor. The solution of each plug-flow-reactor was performed by the LSODE routine described by Radhakrishnan and Hindmarsh (1993). The numerical routines were written in 32-bit C++, and executed on a 233 MHz PC. The model was validated by comparisons with Mulholland et al. (1992), and by direct comparisons with other Chemkin model results for problems representative of the current study.

Figure 12 shows the results of the model in terms of mole fractions for CO and H₂, and the temperature inside the reactor for heat removal rates of about 80 °F/inch (1,050 °C/m), limited by a minimum temperature of 1,250 °F (676 °C). As already indicated, the species approach equilibrium very quickly at the high temperatures found at the combustor inlet. This is evident in the results; note that following a temperature drop at each plug-flow-reactor inlet, both the H₂ and CO concentrations quickly approach steady state levels, as does the temperature. At these high temperatures, the ratio of CO to H₂ concentrations is nearly 4:1. By the time the temperature is about 2,500 °F (1,371 °C), however, the CO and H₂ chemistry becomes rather slow, and the ratio of CO to H₂ is 3.6:1. When the temperature becomes about 1,500 °F (815 °C), the CO and H₂ chemistry is essentially frozen at a CO:H₂ ratio of 1.8:1, which compares well with the experimental data showing CO:H₂ ratios of nearly 2 (Figure 8).

To investigate the effect of the rate of heat removal from the gas on the model's predictions, similar studies were done at heat removal rates of 103 and 125 °F/inch (2,730 and 2,250 °C/m), with the same limiting lower temperature of 1,250 °F. These results are shown in Figure 13. The figure shows that the rate of heat removal does not change the results significantly. That is, the ratio of CO to H₂ using this partial oxidation technique will always be near 2:1.

Conclusions

A gas generator was developed to synthesize the gas emitted from the anode of a molten-carbonate fuel cell. The CO:H₂ ratios were found to be much higher than the equilibrium conditions estimated for the anode gas. The model used to investigate this performance showed that the cause was the quenching of the CO chemistry below 1,500 °F. This resulted in the use of the gas generator for ignition studies of the anode syngas (Gemmen 1998), resulting in a conservative estimate for the ignitability of the true anode syngas.

References

- Carlson, G. 1997. Energy Research Corporation, Danbury, CT. Personal communication.
- Kee, R.J., F.M. Rupley, and J.A. Miller. 1989. *Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics*. Sandia National Laboratory Report, SAND89-8009.
- Kim, T.J., R.A. Yetter, and F. L. Dryer. 1994. New Results on Moist CO Oxidation: High Pressure, High Temperature Experiments and Comprehensive Kinetic Modeling. *Twenty-Fifth Symposium (International) on Combustion*, The Combustion Institute, p. 759-766.
- Gemmen, R.S. 1998. Oxidation of Low Calorific Value Gases — Applying Optimization Techniques to Combustor Design. Presented at the 1998 International Joint Power Generation Conference, Baltimore, MD, August 23-26.
- Mulholland, J.A., A.F. Sarofim, and J.M. Beer. 1992. On the Derivation of Global Ignition Kinetics from a Detailed Mechanism for Simple Hydrocarbon Oxidation. *Combustion Science and Technology* 87: 139-156.
- Radhakrishnan, K., and A.C. Hindmarsh. 1993. *Description and Use of LSODE, the Livermore Solver for Ordinary Differential Equations*. NASA Reference Publication 1327.

Figures

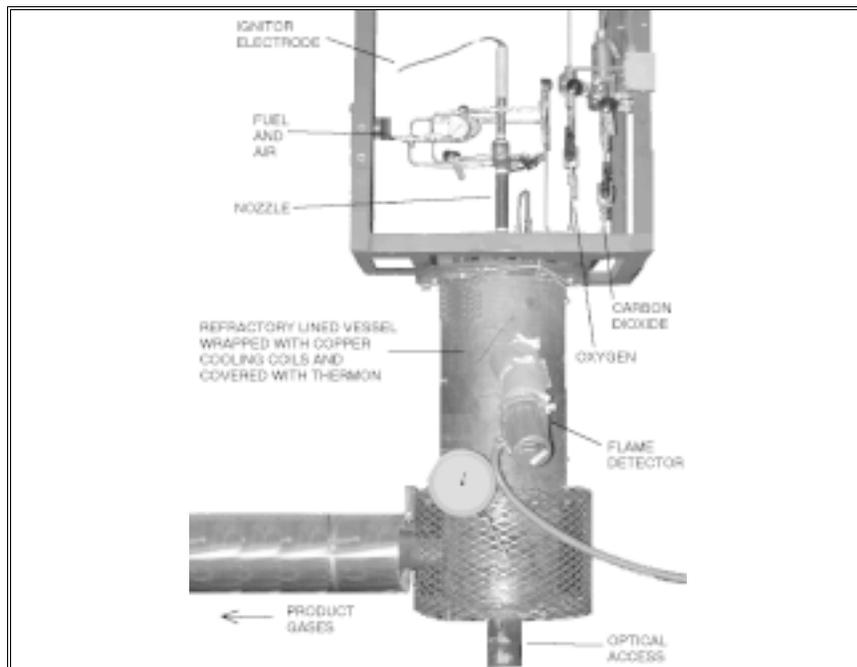


Figure 1. General View of the B27 Gas Generator

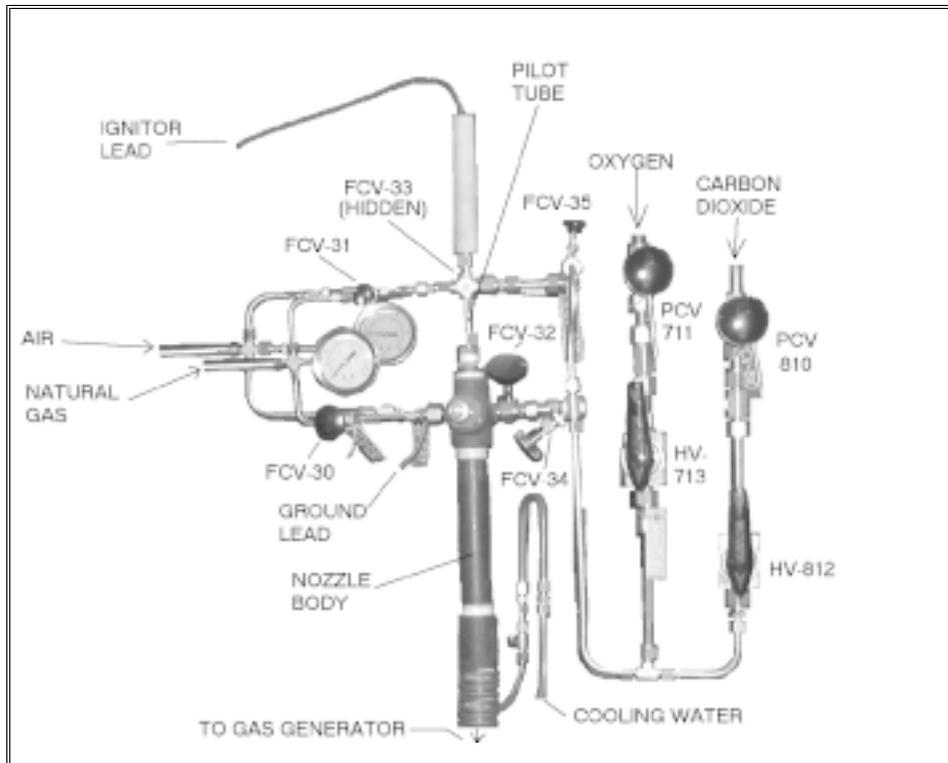


Figure 2a. View of the B27 Gas Generator Nozzle

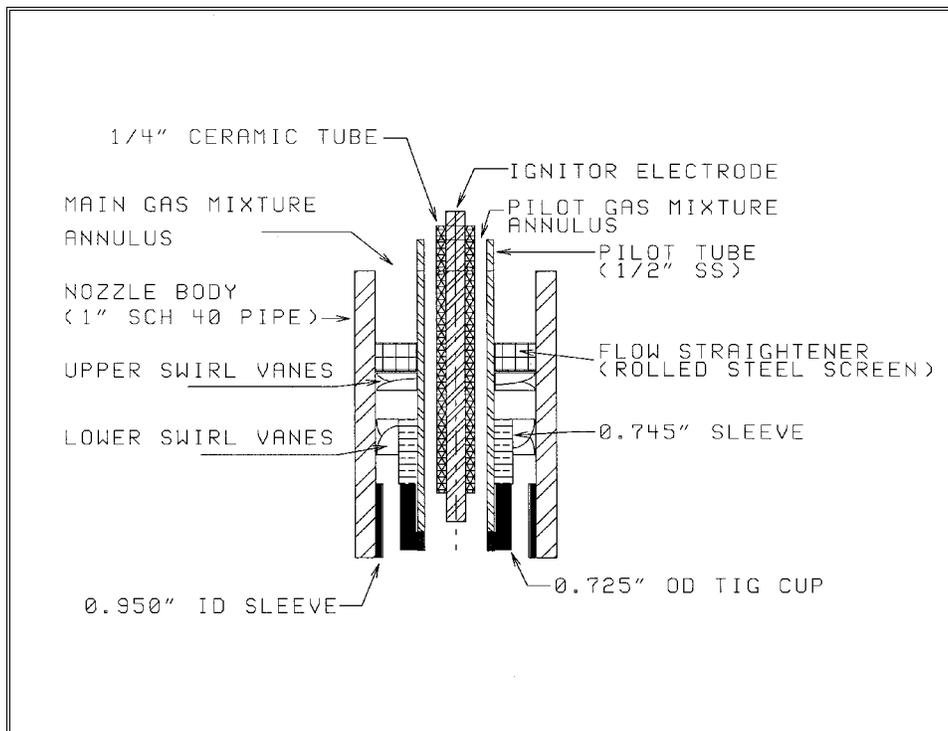


Figure 2b. Detail of Internal Nozzle Geometry
(x-y scales not proportional)

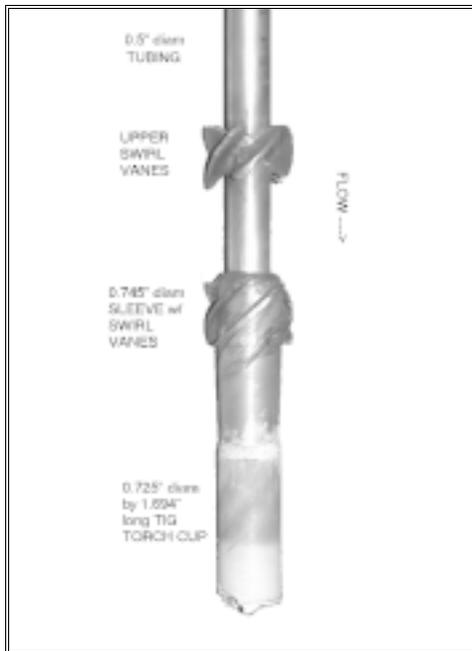


Figure 3. Gas Generator Pilot Tube and Swirl Vane

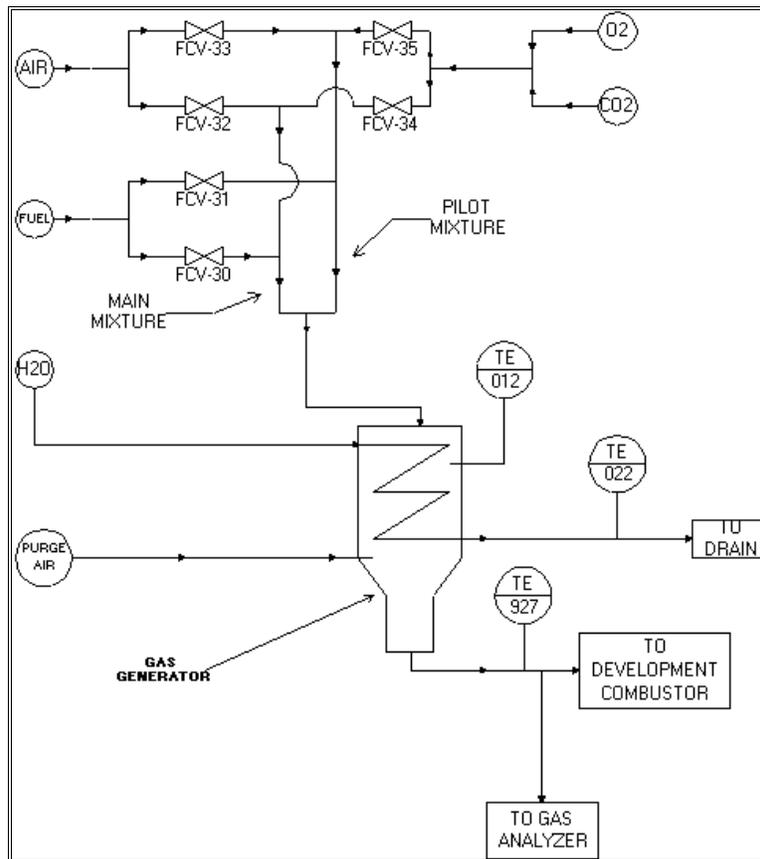


Figure 4. Schematic of Gas Generator

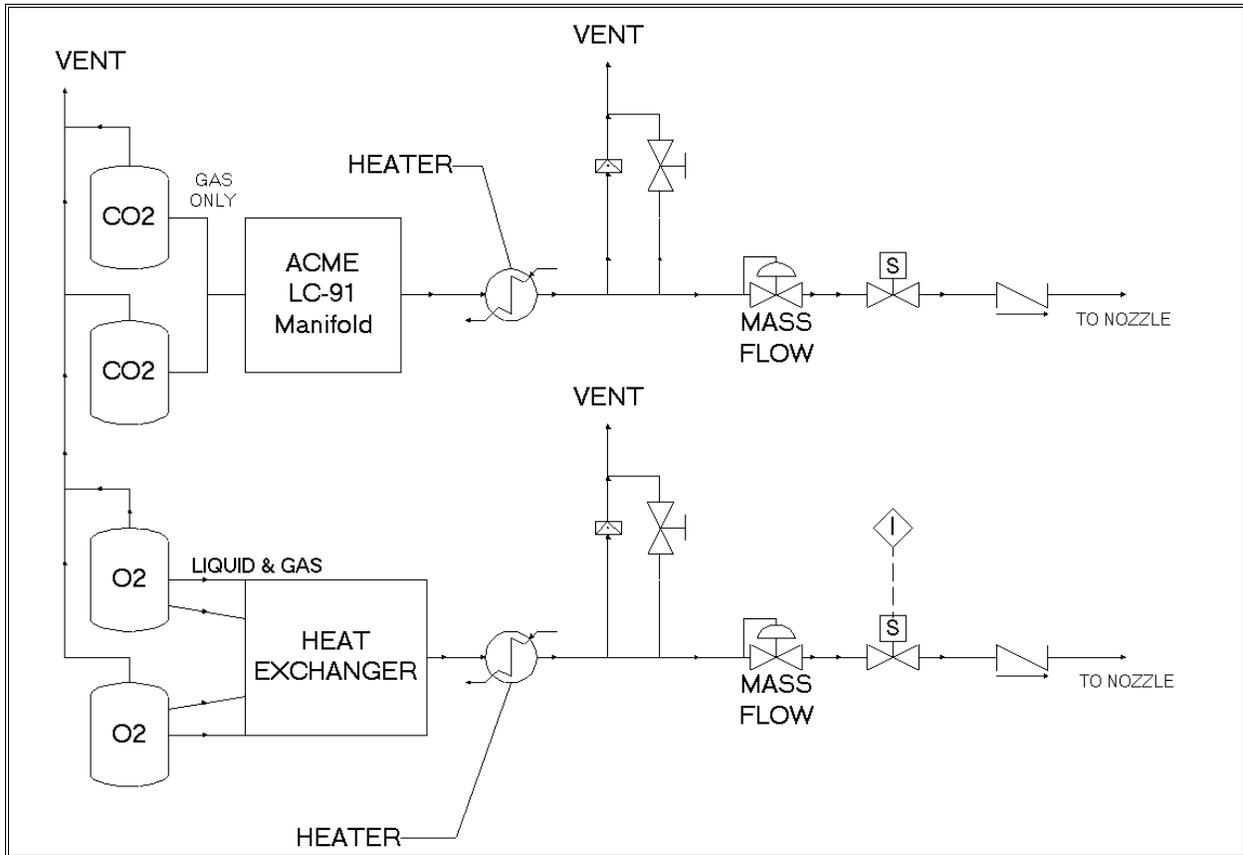


Figure 5. Schematic of Gas Generator Oxygen and Carbon Dioxide Supplies

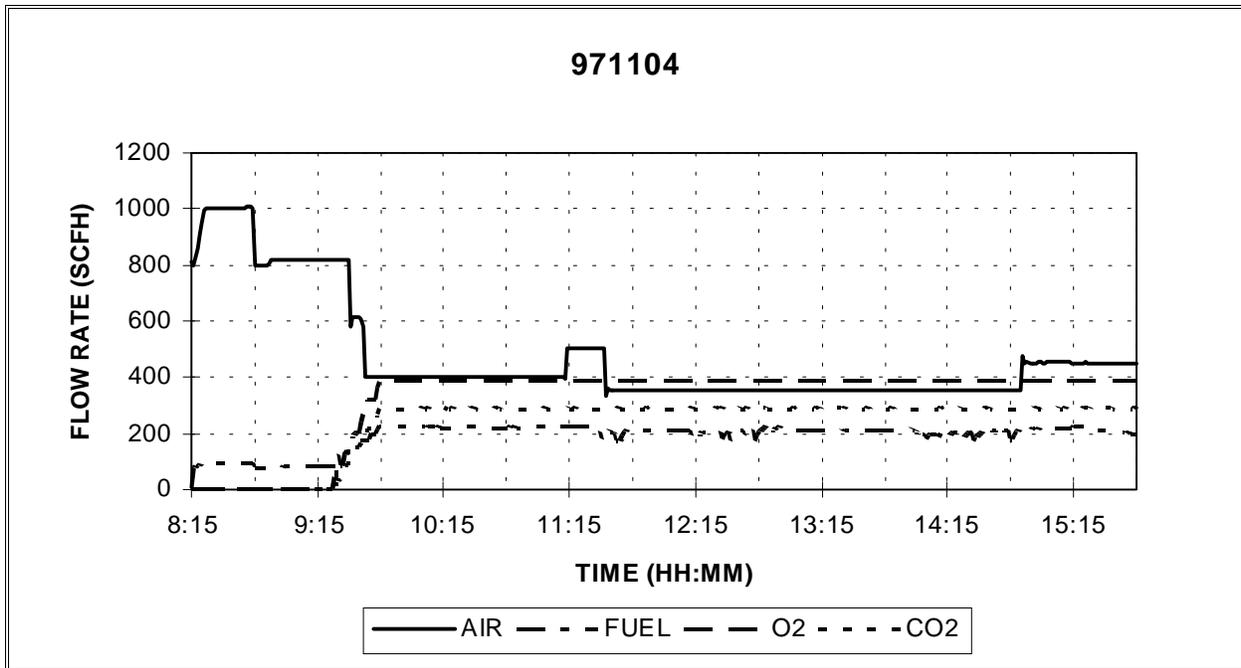


Figure 6a. Flow Rate History of a Typical Run

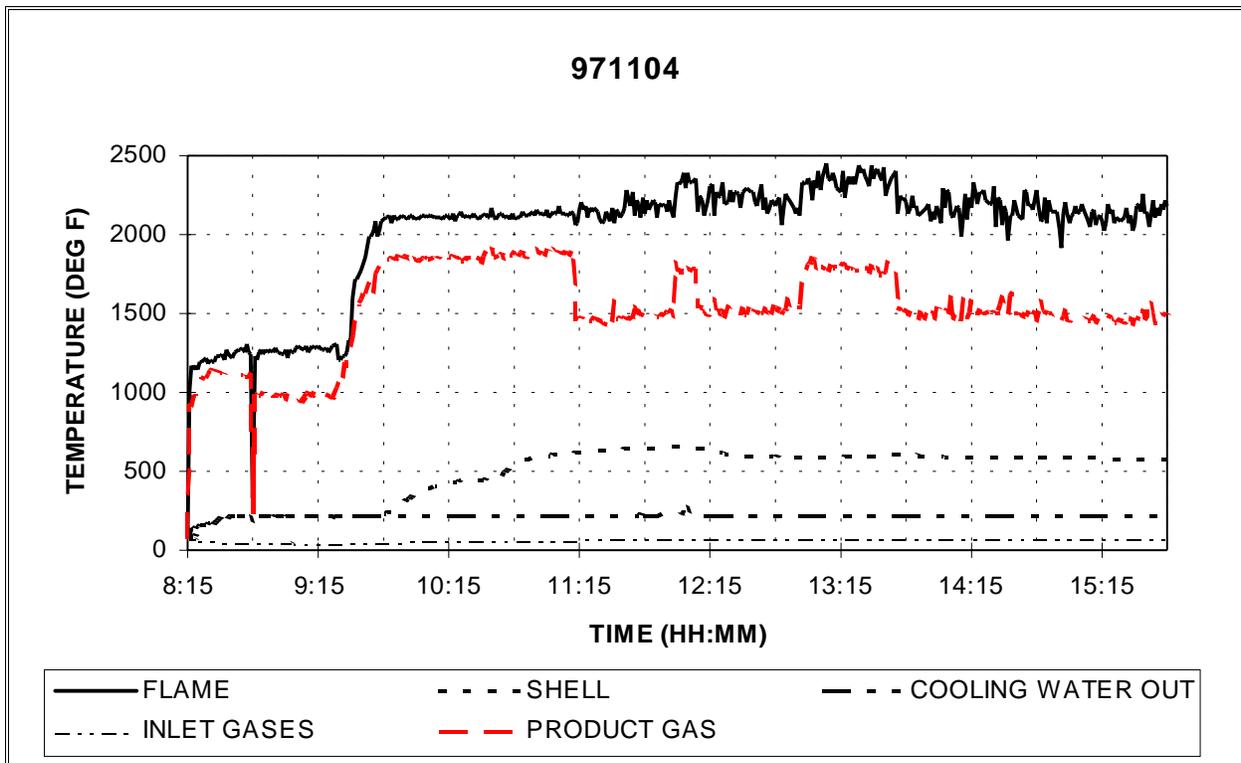


Figure 6b. Temperature History of a Typical Run

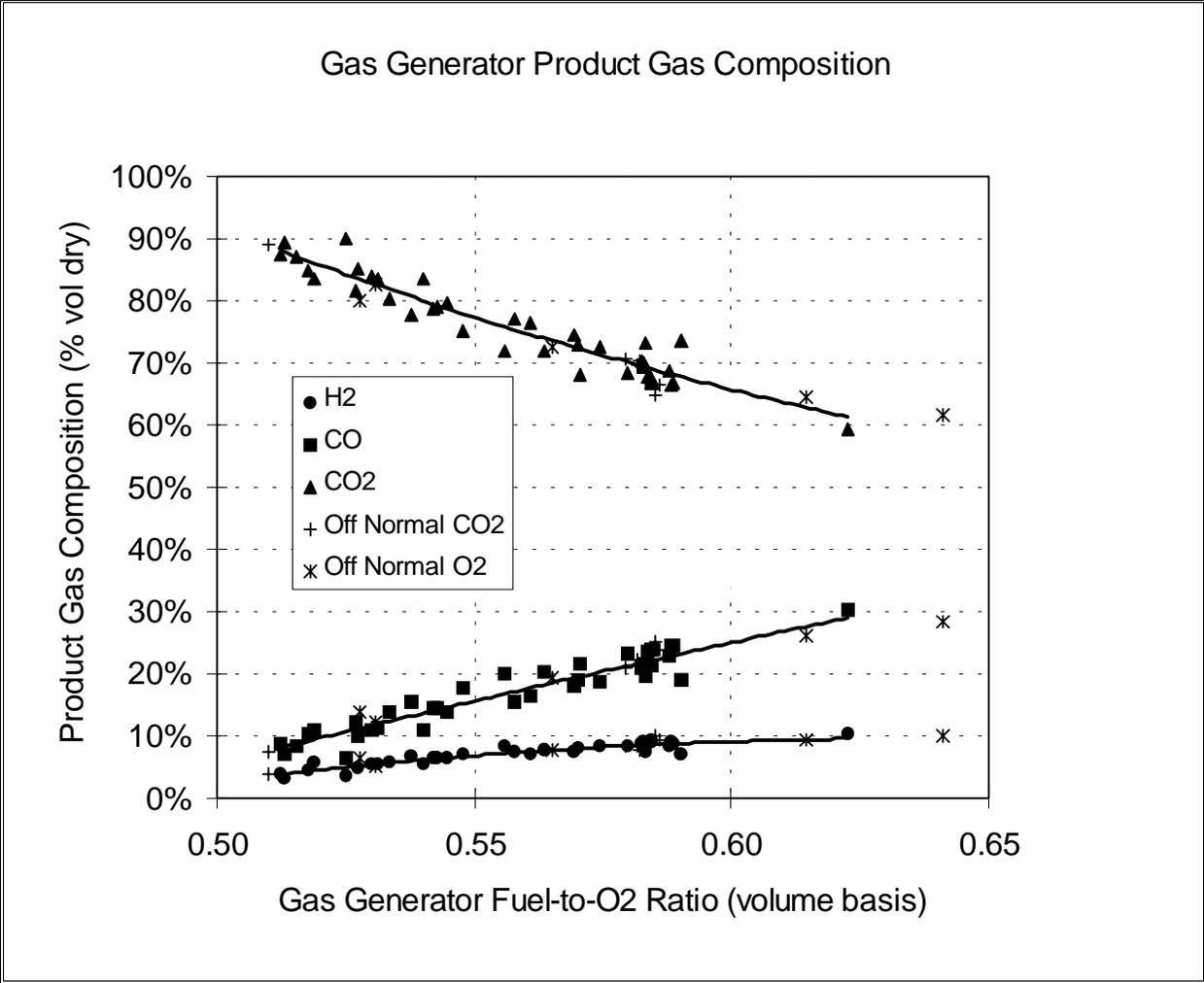


Figure 7. Product Gas Composition Versus Fuel-to-Oxygen Ratio

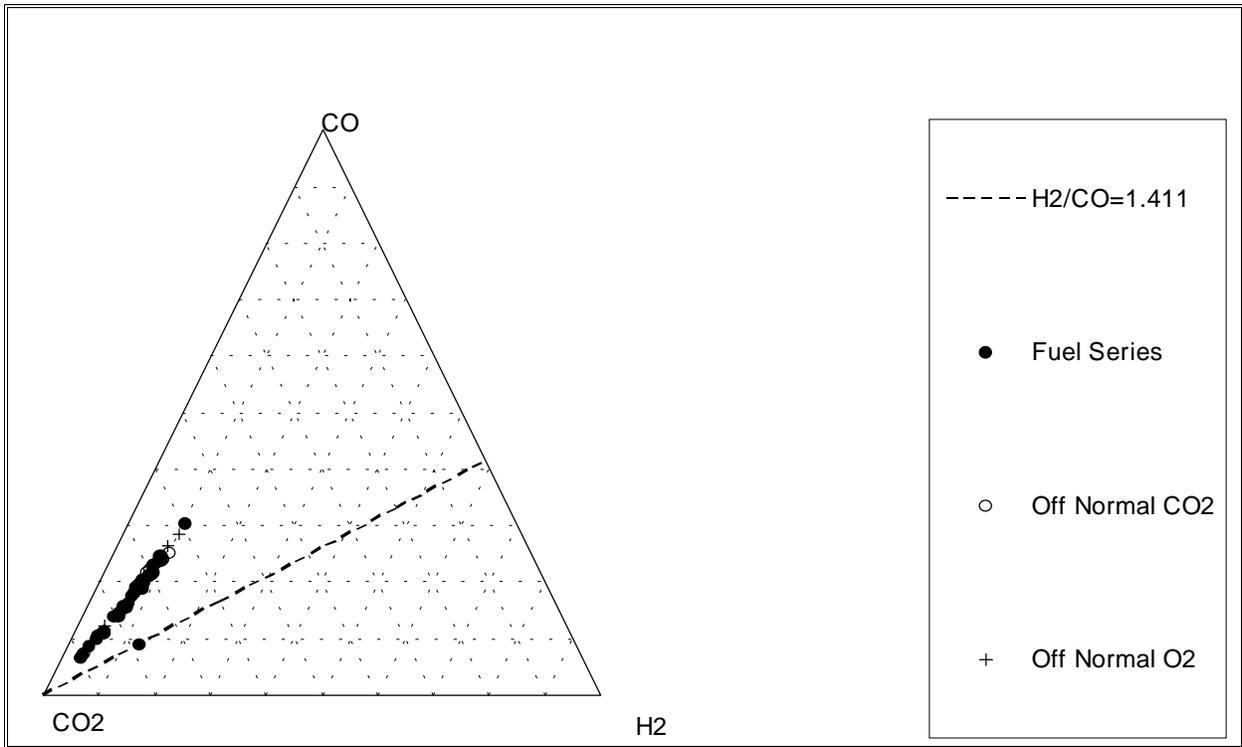


Figure 8. Ternary Plot of Product Gas Compositions (Volume Basis, Dry)

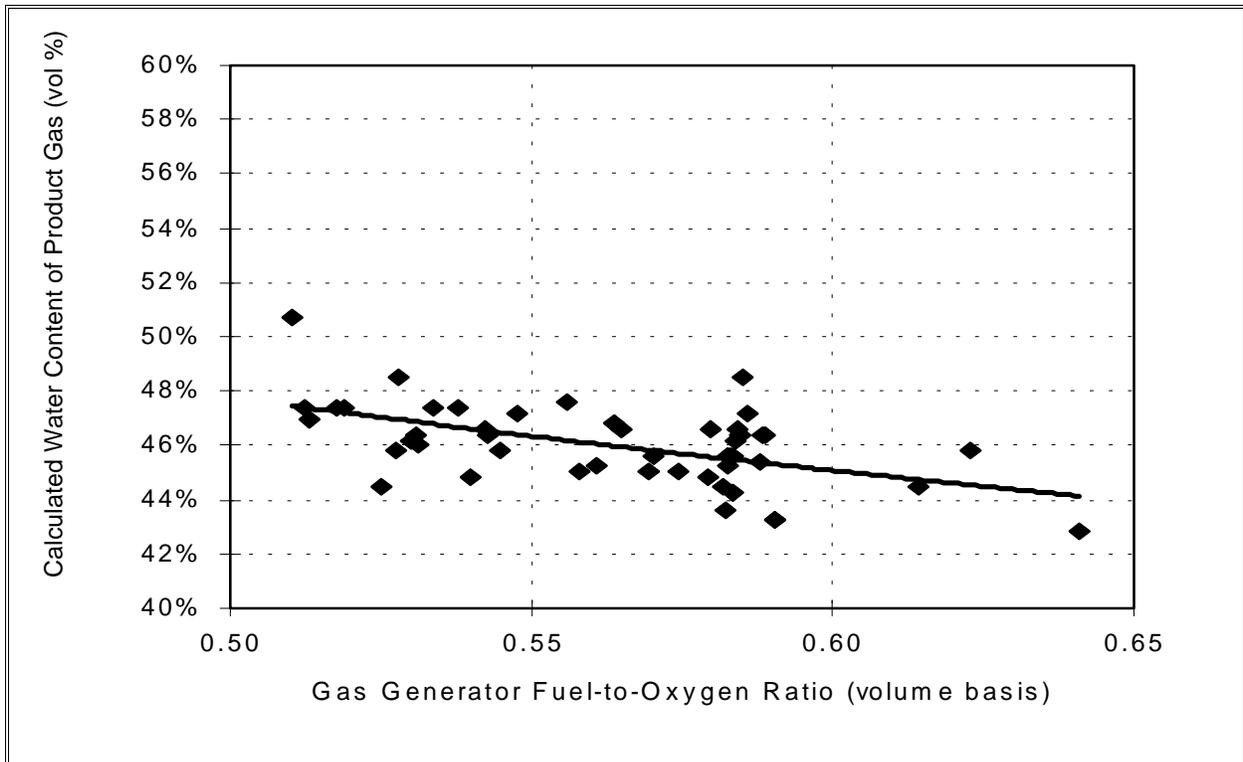


Figure 9. Water Vapor Content of Product Gases

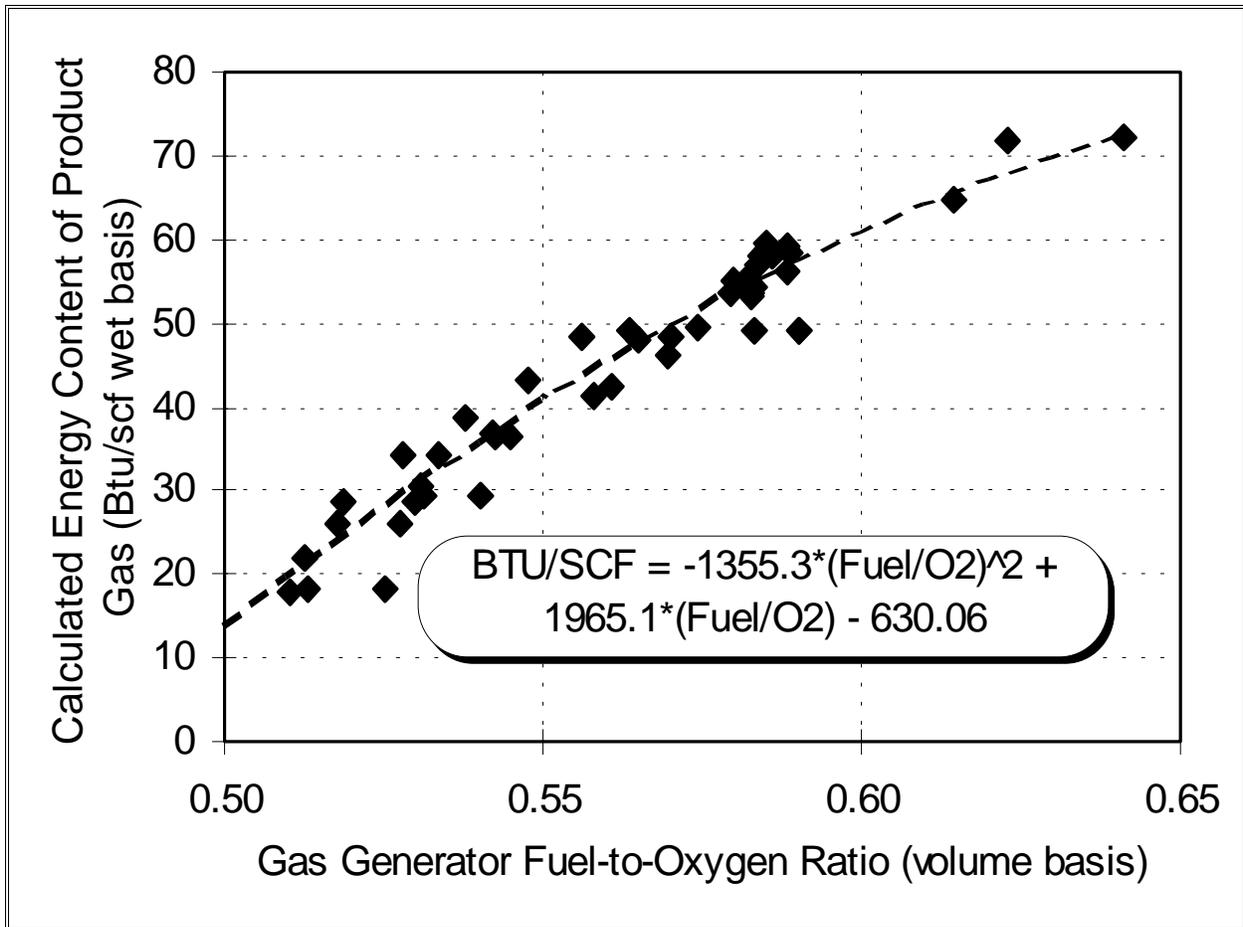


Figure 10. Energy Content (Wet Basis) of Product Gases

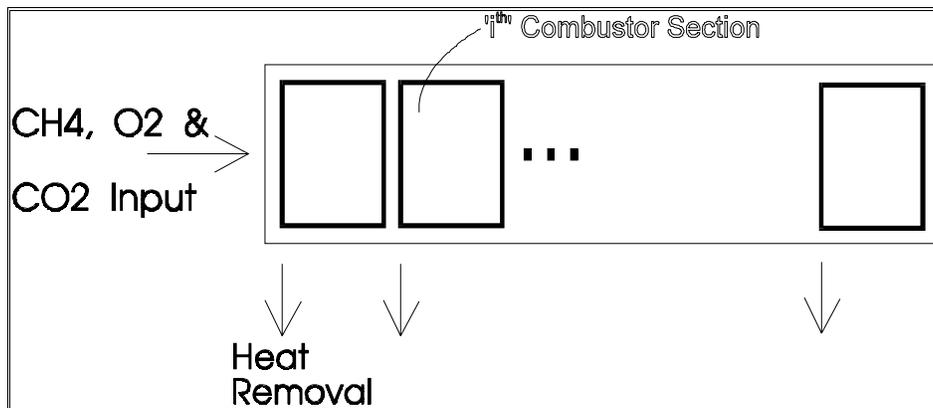


Figure 11. Numerical Model Description

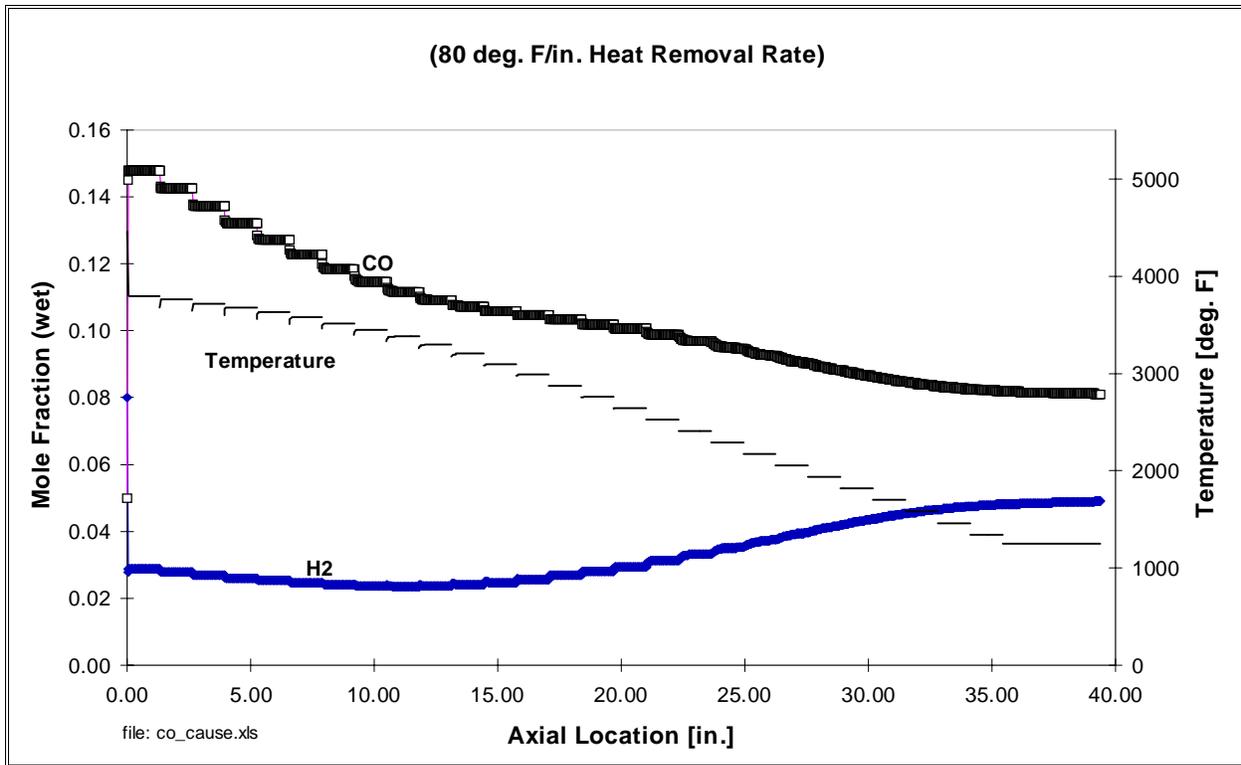


Figure 12. Model Results Showing Quenching of CO and H₂ Inside the Gas Generator

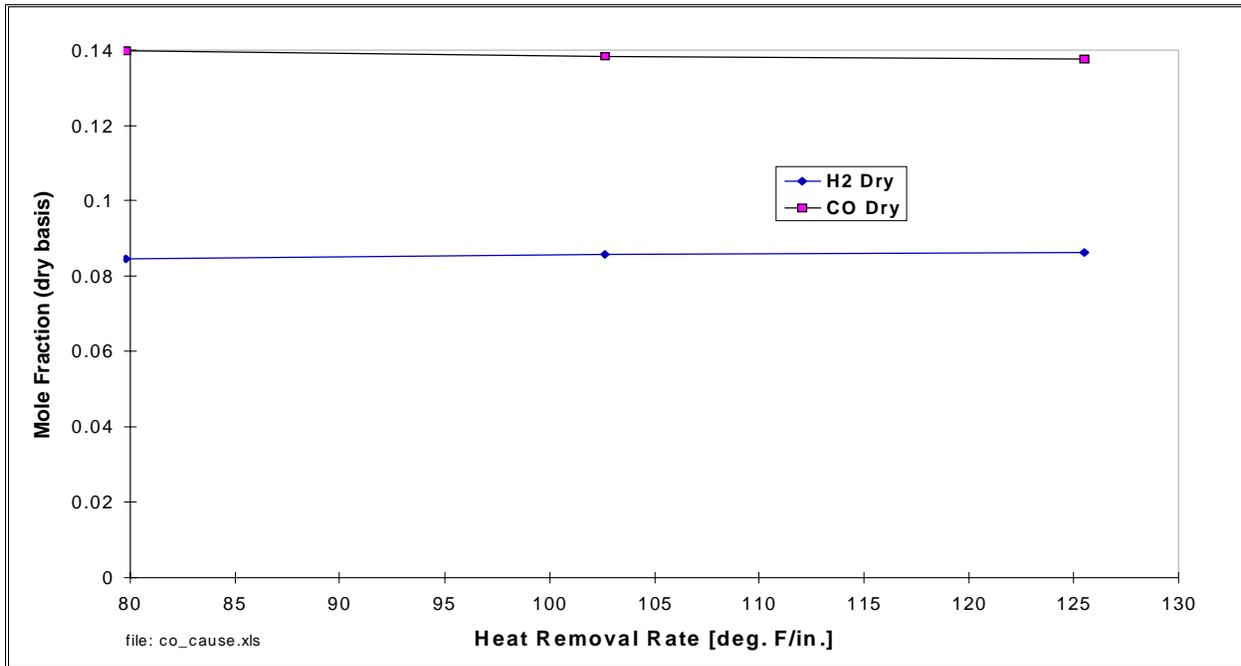


Figure 13. The Effect of Heat Rate on CO and H₂ Predictions

Tables

Table 1. Initial Valve Settings for the Gas Generator Nozzle

Tag Number	Description	Whitey Valve Model	Initial Position (turns open)
FCV-30	Main fuel	SS-1VS4	0.50
FCV-31	Pilot fuel	SS-ORS2	3.10
FCV-32	Main air	SS-1VS6	0.50
FCV-33	Pilot air	SS-ORS2	7.25
FCV-34	Main O ₂ /CO ₂ (a.k.a. "LPM Split")	SS-1VS6	0.25
FCV-35	Pilot O ₂ /CO ₂	SS-ORS2	8.50 (full open)

Table 2. Transition Steps from Start-Up to Normal Gas Generator Operation

Step #	Description	O₂/Fuel Ratio
0	Starting point (800 scf/h air, 75 scf/h fuel)	2.24
1	O ₂ to 40 scf/h	2.78
2	Fuel to 85 scf/h	2.42
3	CO ₂ to 30 scf/h	2.42
4	Fuel to 95 scf/h	2.17
5	O ₂ to 80 scf/h	2.59
6	CO ₂ to 60 scf/h	2.59
7	Fuel to 115 scf/h	2.14
8	O ₂ to 120 scf/h	2.49
9	CO ₂ to 90 scf/h	2.49
10	Fuel to 135 scf/h	2.12
	Open LPM split (FCV-34) to one full turn (total)	
11	O ₂ to 160 scf/h	2.41
12	CO ₂ to 120 scf/h	2.41
13	Air to 600 scf/h	2.11
14	O ₂ to 200 scf/h	2.41
15	CO ₂ to 150 scf/h	2.41
16	Fuel to 155 scf/h	2.10
	Open LPM split by another 1/4 turn	
17	O ₂ to 240 scf/h	2.35
18	CO ₂ to 180 scf/h	2.35
19	Fuel to 175 scf/h	2.08
20	O ₂ to 280 scf/h	2.31
21	CO ₂ to 210 scf/h	2.31
22	Air to 400 scf/h	2.08
	Turn supplement CO ₂ heating elements ON	
23	O ₂ to 320 scf/h (incr. supply press. to 100 psig)	2.30
24	CO ₂ to 240 scf/h	2.30
25	Fuel to 195 scf/h	2.07
	Open LPM another 3/4 turn (two turns total)	
26	O ₂ to 360 scf/h	2.27
27	CO ₂ to 270 scf/h	2.27
28	Fuel to 215 scf/h	2.06
29	O ₂ to 386 scf/h	2.18
30	CO ₂ to 289 scf/h	2.18
31	Fuel to 225 scf/h	2.09
32	Shut off air to GG	1.72
33	Purge air OFF	1.72

Table 3. Analysis of Product Gas Composition

Test Run	Sample Description	Sample Time (hh:mm)	Report Number	Normalized Gas Composition (% Vol Dry)			Feedstock Flow Rates (scf/h)		
				H ₂	CO	CO ₂	Fuel	O ₂	CO ₂
971104	dc inlet sample	15:01	#N/A	8.3%	19.9%	71.8%	215	387	290
971104	dc inlet sample	15:12	#N/A		21.6%	68.1%	220	386	290
971104	dc inlet sample	15:20	#N/A		21.4%	67.4%	226	386	289
971104	dc inlet sample	15:30	#N/A	7.2%	17.6%	75.2%	212	386	289
971104	dc inlet sample	15:38	#N/A		12.4%	81.5%	204	387	289
971104	dc inlet sample	15:44	#N/A		8.5%	87.0%	199	386	290
970808	dc inlet sample	12:50	#N/A	8.0%	19.0%	73.0%	220	386	289
970808	dc inlet sample	13:31	#N/A	7.4%	15.4%	77.2%	215	386	289
970808	dc inlet sample	14:14	#N/A	6.6%	13.8%	79.6%	210	386	289
970808	dc inlet sample	14:58	#N/A	5.4%	11.1%	83.5%	205	386	289
970808	dc inlet sample	15:36	#N/A	3.5%	6.4%	90.0%	203	386	289
970701	dc inlet sample	12:35	0	8.5%	18.9%	72.6%	222	386	289
970625	dc inlet sample	14:46	0	7.2%	16.3%	76.4%	216	386	289
970625	dc inlet sample	15:33	1	5.4%	10.9%	83.7%	205	387	288
970617	dc inlet sample	11:34	1	6.4%	14.4%	79.2%	210	386	289
970617	dc inlet sample	13:38	2	4.8%	9.9%	85.3%	203	385	289
970617	dc inlet sample	15:46	3	7.5%	18.0%	74.6%	219	385	290
970610	dc inlet sample	11:40	1	7.8%	20.3%	71.9%	218	386	290
970610	dc inlet sample	15:58	2	5.7%	10.9%	83.4%	200	386	290
970530	target fuel production	13:43	1	6.7%	15.6%	77.7%	208	386	289
970530	target post catalyst	15:35	4	5.3%	11.0%	83.7%	209	386	291
970521	base conditions	13:10	0	8.7%	21.8%	69.5%	225	386	289
970521	base conditions	13:40	1	8.9%	21.8%	69.4%	225	386	289
970521	case conditions	14:10	2	8.6%	21.0%	70.5%	225	386	288
970520	inlet gas (base?)	14:08	1	7.4%	19.5%	73.1%	225	386	295
970520	inlet (LPM open)	14:40	2	8.5%	22.8%	68.7%	226	385	291
970520	inlet (LPM restricted)	15:10	3	9.3%	23.8%	66.9%	225	386	290
970520	inlet (base)	15:42	4	9.0%	24.6%	66.5%	227	386	289
970520	inlet (restricted cooling)	16:12	5	8.9%	23.4%	67.8%	225	385	289
970520	inlet (base)	16:41	6	9.0%	23.8%	67.2%	225	385	289
970513	base - 20% CO ₂	14:30	5	10.1%	25.2%	64.8%	226	386	231

Table 3. Analysis of Product Gas Composition (continued)

Test Run	Sample Description	Sample Time (hh:mm)	Report Number	Normalized Gas Composition (% Vol Dry)			Feedstock Flow Rates (scf/h)		
				H ₂	CO	CO ₂	Fuel	O ₂	CO ₂
970513	base - 10% CO ₂	14:03	4	9.5%	24.0%	66.5%	226	386	260
970513	base	11:45	0	8.7%	21.4%	69.9%	225	387	286
970513	base	17:00	10	7.3%	19.1%	73.6%	227	384	290
970513	base + 10% CO ₂	12:19	1	8.4%	21.1%	70.5%	224	386	320
970513	base + 20% CO ₂	12:55	2	8.2%	22.1%	69.7%	224	386	348
970513	base + 30% CO ₂	13:28	3	7.8%	21.7%	70.5%	225	386	374
970513	base - 8% O ₂	16:31	9	10.0%	28.5%	61.5%	228	355	288
970513	base - 4% O ₂	16:00	8	9.3%	26.3%	64.4%	227	370	287
970513	base	11:45	0	8.7%	21.4%	69.9%	225	387	286
970513	base	17:00	10	7.3%	19.1%	73.6%	227	384	290
970513	base + 4% O ₂	15:00	6	7.9%	19.4%	72.7%	226	400	288
970513	base + 8% O ₂	15:30	7	6.4%	13.8%	79.8%	222	420	287
970512	base - 15 scf/h fuel	15:06	4	6.5%	14.6%	78.9%	209	386	285
970512	base	14:30	3	8.4%	23.1%	68.5%	225	387	287
970512	base + 15 scf/h fuel	15:55	5	10.2%	30.3%	59.5%	241	386	289
970512	inlet	14:03	2	8.8%	24.5%	66.8%	228	387	287
970423	POC	12:07	0	9.2%	24.0%	66.9%	226	386	286
970423	POC	13:13	1	3.9%	8.7%	87.4%	198	387	282
970423	POC	13:45	2	4.6%	10.4%	84.9%	200	386	286
970423	POC	14:11	3	5.9%	13.9%	80.2%	207	387	282
970423	POC	14:40	4	3.7%	7.3%	89.0%	197	387	208
970423	POC	15:14	5	3.4%	7.1%	89.5%	198	386	275
970423	POC	15:43	6	5.1%	12.2%	82.7%	200	376	289

Appendix

QuickBASIC Code used to calculate water vapor content of product gases by balancing mass flow of oxygen.

```
'-----  
'calculate wet gas composition by balancing O2 mass flows  
'(for DC inlet conditions)  
'-----  
DECLARE FUNCTION O2MassErr! (Vapor!)  
DECLARE SUB SolveH2O ()  
COLOR 7, 1  
CLS  
  
nDim = 7  
DIM SHARED Fuel AS INTEGER  
DIM SHARED O2 AS INTEGER  
DIM SHARED CO2 AS INTEGER  
DIM SHARED CO AS INTEGER  
DIM SHARED H2 AS INTEGER  
DIM SHARED H2O AS INTEGER  
DIM SHARED Total AS INTEGER  
DIM SHARED SCFHperLbMol AS SINGLE  
DIM SHARED Qin(nDim) 'volume flow rates scfh  
DIM SHARED Min(nDim), Mout(nDim) 'mass flows lb/hr  
DIM SHARED Ydry(nDim), Ywet(nDim) 'volume fractions  
DIM SHARED X(nDim) 'Mass Fractions  
DIM SHARED MW(nDim) 'mole wts  
DIM SHARED MWgas 'average MW  
  
InFile$ = "S:\PULSE\B27\LHV\9709\970930\INLET.CSV"  
OutFile$ = "S:\PULSE\B27\LHV\9709\970930\INLET.BAL"  
nSkip = 1  
  
'indices  
Fuel = 1  
O2 = 2  
CO2 = 3  
CO = 4  
H2 = 5  
H2O = 6  
Total = 7
```

'Specify Mole Wt

$MW(\text{Fuel}) = 12.0112 + 4 * 1.00797$

$MW(\text{O}_2) = 2 * 15.9994$

$MW(\text{CO}_2) = 12.0112 + 2 * 15.9994$

$MW(\text{CO}) = 12.0112 + 15.9994$

$MW(\text{H}_2) = 2 * 1.00797$

$MW(\text{H}_2\text{O}) = 2 * 1.00797 + 15.9994$

$\text{SCFHperLbMol} = 379.2$

OPEN InFile\$ FOR INPUT AS #3

IF nSkip > 0 THEN

FOR i = 1 TO nSkip

LINE INPUT #3, junk\$

NEXT i

END IF

OPEN OutFile\$ FOR OUTPUT AS #4

PRINT #4, "Q(Fuel),";

PRINT #4, "Q(O2),";

PRINT #4, "Q(CO2),";

PRINT #4, "Ydry(CO2),";

PRINT #4, "Ydry(CO),";

PRINT #4, "Ydry(H2),";

PRINT #4, "Ydry(O2),";

PRINT #4, "Ywet(CO2),";

PRINT #4, "Ywet(CO),";

PRINT #4, "Ywet(H2),";

PRINT #4, "Ywet(O2),";

PRINT #4, "Ywet(H2O),";

PRINT #4, "TotVol (scfh)"

DO UNTIL EOF(3)

'Input the data

INPUT #3, Q(Fuel), Q(O2), Q(CO2), Ydry(CO2), Ydry(CO), Ydry(H2), Ydry(O2)

'Calculate Common Quantities

$\text{Min}(\text{Fuel}) = Q(\text{Fuel}) * MW(\text{Fuel}) / \text{SCFHperLbMol}$

$\text{Min}(\text{O}_2) = Q(\text{O}_2) * MW(\text{O}_2) / \text{SCFHperLbMol}$

$\text{Min}(\text{CO}_2) = Q(\text{CO}_2) * MW(\text{CO}_2) / \text{SCFHperLbMol}$

$\text{Min}(\text{Total}) = \text{Min}(\text{Fuel}) + \text{Min}(\text{O}_2) + \text{Min}(\text{CO}_2)$

```
'Solve for amount of water to balance O2 mass flows
CALL SolveH2O
```

```
PRINT
  PRINT "Species      Dry      Wet"
PRINT USING "\ \      #.####  #.#### "; "CO2"; Ydry(CO2); Ywet(CO2)
PRINT USING "\ \      #.####  #.#### "; "CO"; Ydry(CO); Ywet(CO)
PRINT USING "\ \      #.####  #.#### "; "H2"; Ydry(H2); Ywet(H2)
PRINT USING "\ \      #.####  #.#### "; "O2"; Ydry(O2); Ywet(O2)
PRINT USING "\ \      #.####  #.#### "; "H2O"; 0; Ywet(H2O)
SLEEP
```

```
'write results out to file
PRINT #4, Q(Fuel); ", ";
PRINT #4, Q(O2); ", ";
PRINT #4, Q(CO2); ", ";
PRINT #4, Ydry(CO2); ", ";
PRINT #4, Ydry(CO); ", ";
PRINT #4, Ydry(H2); ", ";
PRINT #4, Ydry(O2); ", ";
PRINT #4, Ywet(CO2); ", ";
PRINT #4, Ywet(CO); ", ";
PRINT #4, Ywet(H2); ", ";
PRINT #4, Ywet(O2); ", ";
PRINT #4, Ywet(H2O); ", ";
```

```
MWgas = 0
MWgas = MWgas + Ywet(CO2) * MW(CO2)
MWgas = MWgas + Ywet(CO) * MW(CO)
MWgas = MWgas + Ywet(H2) * MW(H2)
MWgas = MWgas + Ywet(O2) * MW(O2)
MWgas = MWgas + Ywet(H2O) * MW(H2O)
```

```
TotVol = Min(Total) * SCFHperLbMol / MWgas
PRINT #4, TotVol
```

```
LOOP
```

```
CLOSE 4
CLOSE 3
```

FUNCTION O2MassErr (Vapor)

'-----
'Calculate Oxygen Mass Balance Error as a function of Water Vapor Content
'-----

$$O2in = Min(O2) + Min(CO2) * MW(O2) / MW(CO2)$$

$$Ywet(CO2) = Ydry(CO2) * (1 - Vapor)$$

$$Ywet(CO) = Ydry(CO) * (1 - Vapor)$$

$$Ywet(H2) = Ydry(H2) * (1 - Vapor)$$

$$Ywet(O2) = Ydry(O2) * (1 - Vapor)$$

$$Ywet(H2O) = Vapor$$

$$MWgas = 0$$

$$MWgas = MWgas + Ywet(CO2) * MW(CO2)$$

$$MWgas = MWgas + Ywet(CO) * MW(CO)$$

$$MWgas = MWgas + Ywet(H2) * MW(H2)$$

$$MWgas = MWgas + Ywet(O2) * MW(O2)$$

$$MWgas = MWgas + Ywet(H2O) * MW(H2O)$$

$$X(CO2) = Ywet(CO2) * MW(CO2) / MWgas$$

$$X(CO) = Ywet(CO) * MW(CO) / MWgas$$

$$X(H2) = Ywet(H2) * MW(H2) / MWgas$$

$$X(O2) = Ywet(O2) * MW(O2) / MWgas$$

$$X(H2O) = Ywet(H2O) * MW(H2O) / MWgas$$

$$O2out = 0$$

$$O2out = O2out + X(CO2) * MW(O2) / MW(CO2)$$

$$O2out = O2out + X(CO) * .5 * MW(O2) / MW(CO)$$

$$O2out = O2out + X(H2) * 0 * MW(O2) / MW(H2)$$

$$O2out = O2out + X(O2) * MW(O2) / MW(O2)$$

$$O2out = O2out + X(H2O) * .5 * MW(O2) / MW(H2O)$$

$$O2out = O2out * Min(Total)$$

$$O2MassErr = O2in - O2out$$

' PRINT O2in; O2out

END FUNCTION

```
SUB SolveH2O
```

```
'-----'
```

```
'use bisection to find volume fraction water that minimizes O2 mass balance
```

```
'error
```

```
'-----'
```

```
    Tol = .001
```

```
    LowH2O = 0
```

```
    HiH2O = 1
```

```
    HiErr = O2MassErr(HiH2O)
```

```
    LowErr = O2MassErr(LowH2O)
```

```
    IF HiErr * LowErr > 0 THEN
```

```
        BEEP: BEEP: BEEP: BEEP: BEEP
```

```
        PRINT "There is no Solution!"
```

```
        PRINT "LowErr="; LowErr
```

```
        PRINT "HiErr="; HighErr
```

```
        MidH2O = 0
```

```
    ELSE
```

```
    DO WHILE ((HiH2O - LowH2O) > Tol)
```

```
        MidH2O = (HiH2O + LowH2O) / 2!
```

```
        MidErr = O2MassErr(MidH2O)
```

```
        IF LowErr * MidErr <= 0 THEN
```

```
            HiH2O = MidH2O
```

```
            HiErr = MidErr
```

```
        ELSE
```

```
            LowH2O = MidH2O
```

```
            LowErr = MidErr
```

```
        END IF
```

```
    LOOP
```

```
END IF
```

```
Ywet(H2O) = MidH2O
```

```
Ywet(CO2) = Ydry(CO2) * (1 - MidH2O)
```

```
Ywet(CO) = Ydry(CO) * (1 - MidH2O)
```

```
Ywet(H2) = Ydry(H2) * (1 - MidH2O)
```

```
Ywet(O2) = Ydry(O2) * (1 - MidH2O)
```

```
END SUB.
```